

we have most probably found the state where the satellite first had a separate existence.

The conditions of stability of a rotating mass of fluid are very obscure, but it seems probable that, if the stability broke down and the mass gradually separated into two parts, then the condition immediately after separation might be something like the unstable configuration described above.

In conclusion, I will add a few words to show that the guiding point on an energy surface need not necessarily move down the steepest path, but may even depart from the bottom of a furrow or move along a ridge. Of this two cases will be given.

The satellite will now be again supposed to be merely an attractive particle.

First, with given moment of momentum, the energy is greater when the axis of the planet is oblique to the orbit. Hence, if we draw an energy surface in which one of the co-ordinate axes corresponds to obliquity, then there must be a furrow in the surface corresponding to zero obliquity. To conclude that the obliquity of the ecliptic must diminish in consequence of tidal friction would be erroneous. In fact, it will appear, in my paper on the "Precession of a Viscous Spheroid," that for a planet of small viscosity the position of zero obliquity is dynamically unstable, if the period of the satellite is greater than twice that of the planet's rotation. Thus the guiding point, though always descending on the energy surface, will depart from the bottom of the furrow.

Secondly. For given moment of momentum the energy is less if the orbit be eccentric, and an energy surface may be constructed in which zero eccentricity corresponds to a ridge. Now, I believe that I shall be able to show, in a future paper, that for small viscosity of the planet the circular orbit is dynamically stable if eighteen periods of the satellite be less than eleven periods of the planet's rotation. This will afford a case of the guiding point sliding down a ridge; when, however, the critical point is passed, the guiding point will depart from the ridge and the orbit become eccentric.

IX. "Researches in Chemical Equivalence. Part III.\* Nickelous and Cobaltous Sulphates." By EDMUND J. MILLS, D.Sc., F.R.S., and J. J. SMITH. Received June 2, 1879.

Although the chemistry of nickel and cobalt is interesting from many points of view, it is more especially attractive from the probable isomerism of these metals. Their combining proportions, in fact,

\* For Part II, see "Proceedings," vol. xxviii, p. 270.

according to the most valuable evidence we possess,\* appear to be entirely the same. We, therefore, thought it very advisable to inquire on what terms they might prove to be mutually equivalent: and the particular equivalence we have examined has been equivalent precipitability of the sulphates, by sodic hydrate, from an aqueous solution.

### I. *Preparation of the Salts.*

The pure cobaltous salt was prepared by converting some excellent commercial crystallized chloride into luteochloride, the process employed having been already described by one of us.† The luteochloride was purified by precipitation with hydric chloride, and the mixture of oxides it left behind on ignition was evaporated with re-distilled hydric sulphate.

The pure nickelous salt was prepared from a sample of nickelous chloride which contained copper, lime, and iron, but no cobalt. The copper present was precipitated with hydric sulphide, and the nickel in the filtrate was precipitated by hydric oxalate, in an acid solution. The nickelous oxalate was washed thoroughly with dilute hydric nitrate, ignited, and the oxide so formed heated with pure hydric sulphate, and so converted into sulphate.

### II. *Method of separating Nickel from Cobalt.*

We had next to select a method for the quantitative separation of nickel from cobalt. The first to which we had recourse was Liebig's,‡ which consists in adding hydric cyanide and potash to the mixed saline solutions, thereby forming nickelopotassic cyanide and potassic cobaltcyanide: these new compounds are boiled with freshly precipitated mercuric oxide, which throws down the nickel as oxide and cyanide. The cobalt in the filtrate is then precipitated as mercurous cobaltcyanide. On the ignition of these precipitates, nickelous oxide and cobaltic oxide are respectively left behind. We converted the oxides into sulphates and weighed them as such. (Throughout the whole of these experiments the nickel and cobalt were always weighed as sulphates.) We found, however, that after the expulsion, by ignition, of the mercury in the precipitates, the oxides were left in so dense and compact a state, that it was only with the greatest difficulty that they could be converted into sulphates. To remedy this, a weighed quantity of pure baric sulphate was added to the liquid before precipitation; the precipitate, becoming mixed with the baric sulphate, was thus spread over a large surface, so that the oxide was obtained in a finely divided state, and easily converted into sulphate.

\* Russell, "Journal of the Chemical Society," (1869), p. 294.

† "Philosophical Magazine," (4), xxxv, p. 245.

"Ann. Ch. Pharm.," lxx, 244.

In the experiments with this process, the nickel was invariably found too high. This was at first thought to be due to alkali which might cling to the precipitated oxide; and, on testing, some potash was actually found in the precipitate, which had been thoroughly washed. To remove this source of error, the nickelous sulphate, instead of being weighed as such, was dissolved in water, excess of ammonia added, and the nickel deposited on a platinum crucible, by means of two Grove's cells.

But the nickel was, with this method, still found too high, and we then thought that the separation had not been perfect. On testing the deposit, a considerable amount of cobalt was, in fact, found in it, and the operation required to be repeated three times before the separation was complete.

The next process we tried was devised by Rose.\* It consists in saturating with chlorine a very dilute solution of the mixed salts, adding baric carbonate in excess, and allowing to stand from twelve to eighteen hours, with occasional shaking. The cobalt then falls as sesquioxide, the nickel remaining in solution.

But the results obtained by this method, as was also the case with Henry's modification of it (which consists in substituting bromine for chlorine) were very variable. In the former case the cobalt was generally found too low, even after standing over eighteen hours; the result appearing to depend a good deal on the liquid being shaken up at regular intervals, which cannot be very conveniently done, during an entire period of eighteen hours. In the latter case, the cobalt was generally found too high, nickel being precipitated along with it.

The last method tried, and the one finally adopted, is due to Gibbs.† In this, the neutral solution of the sulphates is boiled with plumbic peroxide. The cobalt is then precipitated as a higher oxide, while the nickel remains in solution, along with a small quantity of lead. (The author of this process does not claim very great accuracy for it, but we have found it to be of adequate accuracy.)

The manner in which we operated was as follows:—The perfectly neutral solution of the mixed sulphates, was boiled for half an hour with plumbic peroxide, about 7 grms. of the peroxide being taken to 1 grm. of cobaltous sulphate, and the volume of the liquid being about 100 cub. centims. The liquid was then filtered, and the filtrate evaporated to about 20 cub. centims. Some aqueous hydric sulphide was then added, and the small quantity of plumbic sulphide formed filtered off. The solution of nickelous sulphate was then evaporated to dryness in a weighed crucible, ignited, treated with a little hydric sulphate, heated to very dull redness and weighed. The precipitate containing the cobalt, with excess of plumbic peroxide and some sul-

\* "Pogg. Ann.," lxxi, 545.

† "Sill. Am. J.," xiv, 205.

phate, was boiled with hydric chloride until dissolved. Water was then added, and the lead precipitated with hydric sulphate and alcohol. The filtrate from the plumbic sulphate was then evaporated to dryness, heated till the excess of hydric sulphate was driven off, and dissolved in water. A little hydric sulphide was then added, to remove a small quantity of lead still present, the filtrate evaporated to dryness, and the cobaltous sulphate weighed. The plumbic peroxide must, of course, be perfectly pure, because any impurity in it finds its way into the cobalt, and consequently makes that result too high.

In an experiment with this process, .2500 grm. of cobaltous sulphate, and .2500 grm. nickelous sulphate were taken, and the quantities found after the separation were .2505 grm. cobaltous sulphate, and .2490 grm. nickelous sulphate. The estimation of the cobalt is rather a troublesome and tedious process; but when the mixture of nickel and cobalt can be weighed, and the nickel in it estimated, the cobalt being taken by difference, this is an admirable method to employ. The following are some results of the estimation of the nickel in a mixture of .2500 grm. of cobaltous sulphate and .2500 grm. of nickelous sulphate.

	Nickelous sulphate taken.			Found.
(1.)	.....	.2500	.....	.2480
(2.)	.....	„	.....	.2505
(3.)	.....	„	.....	.2490
(4.)	.....	„	.....	.2495
(5.)	.....	„	.....	.2480
Mean....				<hr/> .2490

Probable error of a single determination 0.16 per cent.

### III. *Experiments on Equivalence.*

Having then fixed on the method of separation, 1 per cent. solutions of nickelous and cobaltous sulphates were prepared, and a solution of sodic hydrate, of which 10 cub. centims. were capable of precipitating .8248 grm. of nickelous or cobaltous sulphate. This sodic hydrate was made from sodium, and kept in glass bottles coated internally with a thick layer of paraffin.

A series of nine experiments was made, in which the relative weights of nickelous or cobaltous sulphate present, varied from .1 to .9 grm.; the total weight of nickelous and cobaltous salt, and the volume of the solution being, however, always the same, viz., 1 grm. and 100 cub. centims. The experiments were conducted as follows:—The bottles containing the solutions of the sulphates and the sodic hydrate were immersed in a trough into which there was a constant flow of water to bring them to a constant temperature. The necessary

quantities of nickelous and cobaltous solutions were then carefully measured out, mixed, and the temperature observed. 10 cub. centims. of sodic hydrate were then added, the solution stirred vigorously, and the temperature again observed. The precipitate was then filtered off as quickly as possible (an aspirator being used to facilitate the filtration), and washed, first with cold and then with hot water. Three days' intermittent washing was required to free the precipitate from the undecomposed nickelous and cobaltous salts, cobaltous hydrate having, as is well known, a powerful attraction for cobaltous sulphate, thereby forming a basic salt. After washing, the precipitate was converted into sulphate by treatment with hydric sulphate, and weighed. The mixed sulphates were then dissolved in water, and separated by Gibbs's method, the nickelous sulphate being weighed, and the cobaltous sulphate obtained by difference. It was found that a small quantity of sodic sulphate was always present in the precipitate, the washing having failed to remove it, and this required to be estimated and deducted. For this purpose the nickelous sulphate, after being weighed, was dissolved in water, and the nickel precipitated with baric hydrate. The barium in the filtrate was then removed with hydric sulphate, and the filtrate containing the sodic sulphate evaporated to dryness and weighed. The results obtained are comprised in the following table.

Nickelous salt taken.	Cobaltous salt taken.	Cobaltous salt taken (corr.)	Total precipitate.	Nickelous salt precipitated.	Cobaltous salt precipitated.	Cobaltous salt precipitated (corr.)	Sodic sulphate precipitated.	Temperatures.	Number of experiment.
gram.	gram.	gram.	gram.	gram.	gram.	gram.	gram.	° °	
·1	·9	·8093	·9155	·1050	·8105	·7198	·0105	7-8	I
·2	·8	·7581	·8667	·1980	·6687	·6268	·0110	6-7	II
·3	·7	·6268	·8980	·2765	·6215	·5483	·0135	7-8	III
·4	·6	·5598	·8650	·3510	·5140	·4738	·0105	7-8	IV
·5	·5	·4363	·8885	·4465	·4420	·3783	·0090	7-8	V
·6	·4	·3613	·8-35	·5295	·3340	·2953	·0150	7-7·5	VI
·7	·3	·2808	·8410	·5825	·2615	·2423	·0110	7-7·5	VII
·8	·2	·1408	·8840	·7080	·1760	·1168	0130	8-8·5	VIII
·9	·1	·0483	·8765	·7865	·0900	·0383	0105	7-7·5	IX

In this table the precipitates are all returned as sulphates. The total possible amount of normal sulphate attainable with the constant quantity of sodic hydrate employed having been ·8248 gram., we are able to calculate the entire composition of the precipitate thus:—From its total weight, the amount of sodic sulphate is first subtracted; from the residue the constant quantity ·8248; the remainder, which is the cobaltous sulphate carried down with the hydrate, is deducted as a correction from the cobaltous sulphate originally taken and that which was precipitated, it having no share in the reaction we had to examine. Under “temperature” we give the temperatures of the

reagents before and after mixture. The weight of precipitated sodic sulphate varies but little throughout the experiments, its mean value being .0115 grm. In a special determination, we precipitated, with the usual amount of sodic hydrate, 1.000 grm. of nickelous sulphate alone: after three days' washing, it was found to contain .0115 grm. of sodic sulphate. Hence we infer that when the two sulphates are present together, nickelous hydrate carries down sodic sulphate, cobaltous hydrate carrying down cobaltous sulphate.

#### IV. Discussion.

In the following discussion, it will be understood that we refer to the tabular results already given.

If  $n$  represent a weight of nickelous sulphate taken, and  $\nu$  be the hydrate (calculated to sulphate) obtained from it through precipitation, then we consider  $\phi$  in the expression  $n=\phi\nu$  to represent the *precipitability* of nickelous sulphate: and similarly in  $c=\phi\gamma$ ,  $\phi$  represents the precipitability of cobaltous sulphate. In examining the numbers obtained with the nickelous salt, the best expression we could find for  $\phi$  was  $\phi=(\alpha+\beta n)$ . We first calculated the values of  $\alpha$  and  $\beta n$  from all the determinations, and by the method of least squares, thus obtaining

$$\phi=.98891+.22571n.$$

It is, however, clear that  $\alpha$  cannot be less than unity; moreover, the first weight of nickelous precipitate is somewhat higher than is possible, and we have thought well to reject it. With these amendments we finally obtain

$$\phi=1+.21940n,$$

with a probable error of .02558 for a single determination, or .00904 for eight determinations. Hence we infer that the *precipitability of nickelous sulphate is directly proportional to its mass*.

In the case of cobaltous sulphate, on the other hand, no such law holds good. After a very careful examination of the numbers, we could not find any satisfactory evidence of a change in precipitability with its mass, and consequently represent  $\phi$  as a constant. The mean value of  $\phi$  is in this case 1.1845, with a probable error of .02792 on a single determination, or .00931 for nine determinations. Thus  $\phi$  is about equally well ascertained in both cases.

Our two equations may now be written

$$\left. \begin{aligned} n &= (+.21940\ n)\nu \\ c &= 1.1845\gamma \end{aligned} \right\}$$

In order to calculate in what proportions the two sulphates are equally precipitable, we have

$$1+.21940n=1.1845,$$

whence  $n = \cdot 84093$ . The two sulphates, then, are equally precipitable when the weight taken of each is  $\cdot 84093$  grm.

To calculate in what proportions the two sulphates must be mixed, to give equal weights of precipitate, we have

$$\left. \begin{aligned} \frac{n}{c} &= \frac{(1 + \cdot 21940 n) \nu}{1 \cdot 1845 \gamma} \\ n &= 1 - c \end{aligned} \right\}$$

If we put  $\frac{\nu}{\gamma} = 1$ , and combine these equations, the result is a quadratic, one of whose solutions is  $c = \cdot 5168$ , and consequently  $n = \cdot 4832$ . Using these values in the primitive equations, the results are,  $\gamma = \cdot 4363$ ,  $\nu = \cdot 4369$ , which we may regard as substantially equal.

A highly important chemical relation is disclosed when the two sulphates are so conditioned as to be equally precipitable. We have seen that this is the case when  $n = c = \cdot 84093$ . Now the reciprocal of  $\cdot 84093$  is  $1 \cdot 1892$ ,—a number differing by only the small amount of  $0 \cdot 40$  per cent. from  $1 \cdot 1845$ , or  $\phi \gamma$ . Deduced, as these values both are, from a series of experiments, we cannot hold their connexion to be accidental. It may be thus expressed in symbols,—

$$n = \frac{1}{\phi \gamma} = \frac{\gamma}{c};$$

or we may state the relation thus:—*For an equal weight, nickelous and cobaltous sulphates are equally precipitable; the attraction of the one towards the reagent being then inverse to that of the other.*

In order to ascertain whether this function admits of extension to other weights than  $\cdot 84093$  grm. of the sulphates, we doubled all the masses in one of our previous experiments (V in the table), and determined the chemical effect. The results were

Uncorrected total precipitate . . . . .	1·7840 grm.	}
Containing of nickelous sulphate ..	0·8925	„ }
The halves of these are . . . . .	0·8920	„ }
	0·4463	„ }
Figures nearly identical with. . . . .	0·8975	„ }
	0·4465	„ }

derived from Experiment V. By doubling the mass, we thus produce double the chemical effect. It is probable that this law is general; and, therefore, we infer that the reciprocal function we have noticed may apply to multiples of the weights to which, in our particular case, it specially appertained. Bearing in mind that  $\text{NiSO}_4 = \text{CoSO}_4 = 154 \cdot 65$ , we accordingly write the function thus :

$$\phi(\text{NiSO}_4) = (\phi \text{CoSO}_4)^{-1}.$$

If we imagine some reaction—such, for example, as the combination of colouring matter with a tissue—influenced in one set of experiments by nickelous sulphate, and in an altogether different set by an equal weight of cobaltous sulphate, we can hardly conceive any ground for the development of a reciprocal function, such as we have experimentally traced. On the other hand, it seems reasonable to suppose that, when two bodies are simultaneously confronted with a single reagent, they both contend for its effect. Thus a chemical antagonism may arise between them by virtue merely of their being together; and thence the reciprocal function. So far as we are aware, the only other chemical function of the kind, hitherto investigated, is to be found in Chiżyński's\* examination of the partial precipitation, by ammoniac phosphate, of mixed calcic and magnesian chlorides. That chemist arrived at the conclusion, for which we consider his evidence to be adequate, that “equal masses of calcic and magnesian chlorides have always equal, but oppositely active, coefficients of affinity.”

X. “On the Formation of Hydrocyanic Acid in the Electric Arc.” By JAMES DEWAR, M.A., F.R.S., Professor of Chemistry to the Royal Institution. Received June 5, 1879.

A series of experiments favouring the conclusion that the so-called carbon lines are invariably associated with the formation of acetylene† induced me to make some experiments to ascertain whether this substance can be extracted from the electric arc, which invariably shows this peculiar spectrum at the positive pole, when it is powerful and occasionally intermittent. For this purpose the carbons were used in the form of tubes, so that a current of air could be drawn by means of an aspirator through either pole, and the products thus extracted from the arc, collected in water, alkalies, and other absorbents. Gases may be led through one of the poles, and suction induced through the other, in order to examine their effect on the arc.

The following experiments record the results obtained by means of the Siemens and de Méritens's magneto-machines.

*Experiment 1.*—Drew a current of air by an aspirator through the drilled negative carbon, and passed the gases through potash, and iodide of potassium, and starch paste; found no nitrites; potash contained sulphides.

*Experiment 2.*—Hydrogen led in by the positive pole and the gases extracted as above, gave the well-known acetylene compound with

\* Ann. Ch. Pharm., Supp. iv, 226—253.

† As suggested by Plücker, Ångström, and Thalén.